1.0

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The metal-metal bonded complexes $[Co_2(CO)_6L_2]$ (L = P(n-Bu)$_3$, P(OPh)$_3$) and $[Fe(\eta^5-C_5H_5)(CO)_2Co(CO)_3(P(OPh)_3)]$ all undergo efficient ($\phi > 0.1$ at 355 nm) photochemical metal-metal bond cleavage to produce reactive 17-valence electron $[Co(CO)_3L]$ fragments. In the presence of 1-pentene no alkene isomerization is found for L = P(n-Bu)$_3$; low, but significant, photocatalytic activity is found for L = P(OPh)$_3$ or when the P(n-Bu)$_3$ complex is irradiated in the presence of P(OMe)$_3$. The $[Co(CO)_3L]$ precursors are strikingly more active when irradiation
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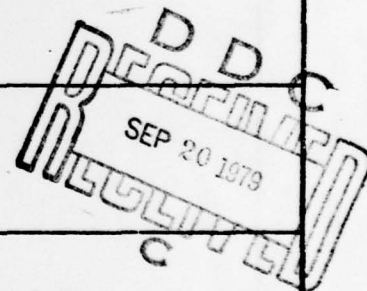
is carried out in the presence of $HSiEt_3$, a hydride source. Both alkene isomerization and n-pentane formation are observed, along with small quantities of Si-containing products. The $[Fe(\eta^5-C_5H_5)(CO)_2]$ radical photogenerated independently from $[Fe(\eta^5-C_5H_5)_2(CO)_4]$ is not active under any conditions used thus far. The activity of 17-valence electron radicals in this application is $[Co(CO)_3(P(OPh)_3)] > [Co(CO)_3(P(n-Bu)_3)] > [Fe(\eta^5-C_5H_5)(CO)_2]$. These species are not themselves effective catalysts but do seem to react with $HSiEt_3$ to form catalytically active, mononuclear Co-hydride complexes.

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TECHNICAL REPORT NO. 18

Photoactivation of Cobalt Carbonyl Catalysts:

Generation of Reactive Mononuclear Fragments from

Dinuclear, Metal-Metal Bonded Complexes

by

Carol L. Reichel and Mark S. Wrighton

Prepared for Publication

in the

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Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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Photoactivation of Cobalt Carbonyl Catalysts: Generation of Reactive Mononuclear Fragments From Dinuclear, Metal-Metal Bonded Complexes

Abstract: The metal-metal bonded complexes $[Co_2(CO)_6L_2]$ (L = P($\underline{n}$-Bu)$_3$, P(OPh)$_3$) and $[Fe(\eta^5-C_5H_5)(CO)_2Co(CO)_3(P(OPh)_3)]$ all undergo efficient ($\Phi > 0.1$ at 355 nm) photochemical metal-metal bond cleavage to produce reactive 17-valence electron $[Co(CO)_3L]$ fragments. In the presence of 1-pentene no alkene isomerization is found for L = P($\underline{n}$-Bu)$_3$; low, but significant, photocatalytic activity is found for L = P(OPh)$_3$ or when the P($\underline{n}$-Bu)$_3$ complex is irradiated in the presence of P(OMe)$_3$. The $[Co(CO)_3L]$ precursors are strikingly more active when irradiation is carried out in the presence of HSiEt$_3$, a hydride source. Both alkene isomerization and $\underline{n}$-pentane formation are observed, along with small quantities of Si-containing products. The $[Fe(\eta^5-C_5H_5)(CO)_2]$ radical photogenerated independently from $[Fe_2(\eta^5-C_5H_5)_2(CO)_4]$ is not active under any conditions used thus far. The activity of 17-valence electron radicals in this application is $[Co(CO)_3(P(OPh)_3)] > [Co(CO)_3(P(\underline{n}$-Bu)$_3)] > [Fe(\eta^5-C_5H_5)(CO)_2]$. These species are not themselves effective catalysts but do seem to react with HSiEt$_3$ to form catalytically active, mononuclear Co-hydride complexes.
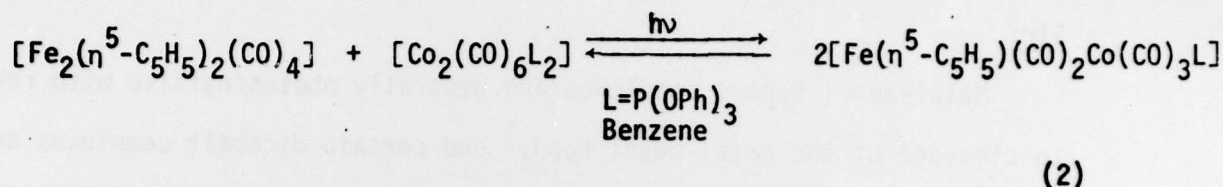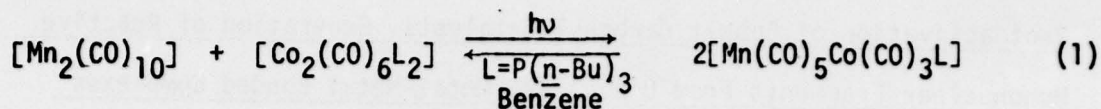
Photoactivation of Cobalt Carbonyl Catalysts: Generation of Reactive Mononuclear Fragments From Dinuclear, Metal-Metal Bonded Complexes

Sir:

Metal-metal bonded complexes are generally photosensitive with respect to cleavage of the metal-metal bond,[1] and certain dicobalt complexes are known[2] to be hydroformylation catalyst precursors under thermal conditions. We report herein our preliminary results concerning the photogeneration of catalytically active mononuclear cobalt carbonyl fragments from dinuclear, metal-metal bonded complexes. The results illustrate the potential utility of photoinduced metal-metal bond cleavage in probing catalytic mechanisms and in initiating catalytic chemistry under thermal conditions where there would be no reaction without light activation. The complexes studied thus far are $[Co_2(CO)_6L_2]$ (L = $P(\underline{n}\text{-Bu})_3$, $P(OPh)_3$) and $[Fe(\eta^5\text{-}C_5H_5)(CO)_2Co(CO)_3(P(OPh)_3)]$,[3] and the catalytic probe chemistry has been reaction of 1-pentene/$HSiEt_3$ mixtures. The cobalt systems have been chosen for study because it is believed that the dinuclear $[Co_2(CO)_6(P(\underline{n}\text{-Bu})_3)_2]$ actually forms mononuclear $[HCo(CO)_3(P(\underline{n}\text{-Bu})_3]$ under hydroformylation conditions.[2] The ability to photogenerate $[Co(CO)_3L]$ under mild thermal conditions offers an opportunity to gain insight into the mechanisms of cobalt carbonyl catalyzed reactions.

All three complexes studied here undergo efficient photochemical cleavage of the metal-metal bond, as reflected in the photochemistry that we find, equations (1) and (2). $[Mn_2(CO)_{10}]$[4]

$$[Mn_2(CO)_{10}] + [Co_2(CO)_6L_2] \xrightleftharpoons[\substack{L=P(\underline{n}\text{-Bu})_3 \\ \text{Benzene}}]{h\nu} 2[Mn(CO)_5Co(CO)_3L] \qquad (1)$$

$$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4] + [Co_2(CO)_6L_2] \xrightleftharpoons[\substack{L=P(OPh)_3 \\ \text{Benzene}}]{h\nu} 2[Fe(\eta^5\text{-}C_5H_5)(CO)_2Co(CO)_3L]$$

$$(2)$$

and $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]^5$ are known to undergo efficient metal-metal bond cleavage, and the photoinduced formation of heterodinuclear complexes is believed to result from coupling of two different 17-valence electron radicals. The forward and reverse photoreactions represented in equations (1) and (2) are chemically clean, and quantum yields for near-ultraviolet light induced cleavage of the metal-metal bonds are all >0.1.

Irradiation of $[Co_2(CO)_6L_2]$ in the presence of 1-pentene in benzene or $\underline{n}$-octane solution results in little net reaction of any kind. The disappearance of the Co-Co bonded species is very slow, particularly for L = $P(\underline{n}\text{-Bu})_3$. Presumably, the Co-Co bond is cleaved efficiently, but recoupling of the $[Co(CO)_3L]$ fragments obtains to result in little net chemical change. Irradiation of the Fe-Co bonded species under the same conditions results in the redistribution reaction shown in equation (2). Table I shows the effect on 1-pentene by irradiating the $[Co_2(CO)_6L_2]$ species. For L = $P(\underline{n}\text{-Bu})_3$ there is no detectable reaction in 94 h, but for L = $P(OPh)_3$ there is considerable alkene isomerization and a small amount of $\underline{n}$-pentane forms. Further, adding $P(OMe)_3$ to a $1\underline{M}$ 1-pentene solution containing $[Co_2(CO)_6(P(\underline{n}\text{-Bu})_3)_2]$ results in photocatalytic activity comparable to that found for the $[Co_2(CO)_6(P(OPh)_3)_2]$ complex.
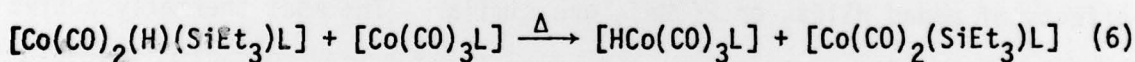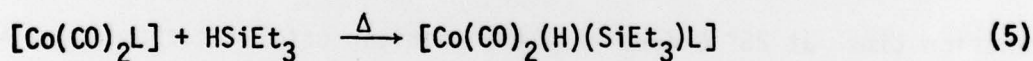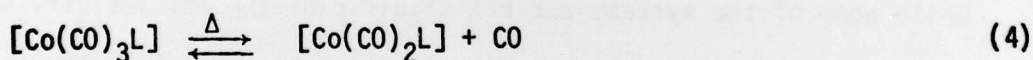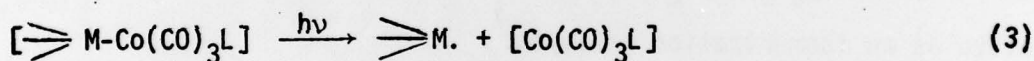
Addition of $HSiEt_3$ to the 1-pentene solutions dramatically affects the photocatalytic activity, Table II. Under the same conditions, except for the presence of $HSiEt_3$, the photolysis of $[Co_2(CO)_6(P(\underline{n}\text{-}Bu)_3)_2]$ essentially completely equilibrates the linear pentenes to the thermodynamic ratio,[6] whereas no reaction obtains in the absence of the $HSiEt_3$. A significant amount of $\underline{n}$-pentane is formed and small quantities of Si-containing products are also detectable but have not been analyzed quantitatively. The addition of $P(OMe)_3$ further accelerates the photocatalytic activity of the $P(\underline{n}\text{-}Bu)_3$ complex. The effect of added $HSiEt_3$ on the photocatalytic activity of the $[Co(CO)_3P(OPh)_3]$ precursors is equally striking. The heterodinuclear Fe-Co complex is about as active as the homodinuclear precursor. Note that the $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ is essentially non-active and is, of course, the homodinuclear source of the 17-valence electron radical $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]$. However, the related radical, $[Fe(\eta^3\text{-}C_3H_5)(CO)_3]$, is active as an isomerization catalyst.[7]

While none of the systems exhibit significant thermal activity on the same time scale as used in the photochemical experiments, long thermal reaction time at 25° C does result in similar catalytic chemistry, and the effects of added $HSiEt_3$ or $P(OMe)_3$ are similar. The most thermally active species is the $[Co_2(CO)_6(P(OPh)_3)_2]$; the $[Fe(\eta^5\text{-}C_5H_5)(CO)_2Co(CO)_3(P(OPh)_3)]$ is qualitatively less active, but the least active complex is $[Co_2(CO)_6(P(\underline{n}\text{-}Bu)_3)_2]$.

The data suggest that the 17-valence electron radicals $[Co(CO)_3L]$ (L = $P(\underline{n}\text{-}Bu)_3$, $P(OPh)_3$) or $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]$ are not themselves active catalysts for alkene isomerization. However, these species apparently can react with $HSiEt_3$, a hydride source, to give mononuclear hydride catalysts for isomerization and alkene reduction. The enhanced catalytic activity, $\underline{n}$-pentane formation, and formation of Si-containing products strongly implicate such a role for the $HSiEt_3$. Irradiation of metal-metal bonded compounds in the presence of silicon hydrides is known to result in the

formation of silyl- and hydride complexes.[8] Note that $[M_2(CO)_8H_2]$ (M=Mn, Re) can be formed via photolysis of $[M_2(CO)_{10}]$ in the presence of H_2.[9] Ir and uv-vis spectral changes in our system containing $HSiEt_3$ reveal conversion to mononuclear Co complexes, and catalytic activity persists when all metal-metal bonded compounds are exhausted. Molecular H_2 at 2 atm does appear to serve as a source of hydride for $[Co_2(CO)_6(P(OPh)_3)_2]$ but the catalytic activity in the presence of 1 $\underline{M}$ 1-pentene is not as great as that found with $HSiEt_3$. A priori H_2 should be less active as a hydride source, since the H-H bond is stronger than the Si-H bond. Whether mononuclear hydrides are responsible for reaction in the absence of H_2 or Si-H sources, Table I, is not clear. Our studies of this low activity situation have not been definitive to date.

Mononuclear Co-hydride complexes possibly arise from reaction of 15-valence electron Co-containing species[10] with $HSiEt_3$ followed by hydrogen abstraction according to reactions (3)-(6), not unlike the processes proposed for the

$$[\gtrsim M-Co(CO)_3L] \xrightarrow{h\nu} \gtrsim M\cdot + [Co(CO)_3L] \tag{3}$$

$$[Co(CO)_3L] \underset{\rightleftharpoons}{\overset{\Delta}{}} [Co(CO)_2L] + CO \tag{4}$$

$$[Co(CO)_2L] + HSiEt_3 \xrightarrow{\Delta} [Co(CO)_2(H)(SiEt_3)L] \tag{5}$$

$$[Co(CO)_2(H)(SiEt_3)L] + [Co(CO)_3L] \xrightarrow{\Delta} [HCo(CO)_3L] + [Co(CO)_2(SiEt_3)L] \tag{6}$$

photochemical formation of $[M_2(CO)_8H_2]$.[9,11] That reaction (4) is crucial is consistent with our finding that 10 psi CO pressure effectively suppresses photocatalytic activity.

Hydrides like that indicated in equation (6) are known catalysts for alkene reactions.[12] Independent preparation[13] of $[HCo(CO)_3P(OPh)_3]$ by addition of $HBF_4 \cdot Et_2O$ to $Na[Co(CO)_3P(OPh)_3]$ in tetrahydrofuran (THF) solution has been carried out, and we find thermal catalytic chemistry (isomerization and alkene reduction at 25°C in $HSiEt_3$/1-pentene, 1.4 $\underline{M}$ each, in THF), and the distribution of products is similar to that found from irradiating $[Co_2(CO)_6(P(OPh)_3)_2]$ under the same conditions. We find that the $[HCo(CO)_3P(OPh)_3]$

has an intense ir absorption at 1992 cm^{-1} (THF), and that at 25°C the complex decomposes[13] to form $[Co_2(CO)_6(P(OPh)_3)_2]$ (1978 cm^{-1}) in THF solution. Further, the catalytic activity of our THF solutions of $[HCo(CO)_3P(OPh)_3]$ is enhanced (~factor of three in rate) by near-uv irradiation. This last result would indicate that our photocatalytic experiments beginning with $[Co_2(CO)_6L_2]$ likely have a component of light-accelerated catalysis by mononuclear compounds. Consistent with this conclusion we find that ~15 min of irradiation of $[Co_2(CO)_6(P(OPh)_3)_2]$ followed by dark reaction yields catalytic chemistry at a rate substantially lower than with continuous irradiation. Comparison of relative dark and light rates accords well with the dark vs. light rates when $[HCo(CO)_3P(OPh)_3]$ is used.

Preliminary results using 1/1 DSiEt$_3$/1-pentene with $[Co_2(CO)_6(P(OPh)_3)_2]$ as the photocatalyst reveals the rapid formation of HSiEt$_3$ (detected by pmr and gc mass spec) accompanying formation of pentane and _cis_- and _trans_-2-pentene. The deuterium is found in all of the hydrocarbons. This experiment confirms an important role for the Si-H(D) system and adds further to the understanding of the mechanism. Thus a Co species containing alkene, hydride, and the tri-alkylsilyl group is implicated in the catalytic cycle. Inasmuch as we do observe significant amounts of alkane product it is reasonable that a key species is in fact $[H_2Co(CO)_2(SiEt_3)L]$ from oxidative addition of HSiEt$_3$ to $[HCo(CO)_3L]$ or from disproportionation of the 17-valence electron species $[HCo(CO)_2(SiEt_3)L]$ indicated in equation (5).

Data in Tables I and II reveal that the ordering of the activity of the three 17-valence electron radicals is $[Co(CO)_3 P(OPh)_3] > [Co(CO)_3 P(\underline{n}\text{-Bu})_3] > [Fe(\eta^5\text{-}C_5H_5)(CO)_2]$. The lower thermal activity of the Fe-Co system compared to $[Co_2(CO)_6(P(OPh)_3)_2]$ is logically a consequence of the more inert metal-metal bond. The effect of added P(OMe)$_3$ on the activity of the P($\underline{n}$-Bu)$_3$ complex is in accord with the notion that the photogenerated $[Co(CO)_3L]$ radicals are substitution labile,[10] and the various substituted radicals will have a different reactivity towards HSiEt$_3$.[14] The activity of the systems studied do

not seem to be great under the conditions employed, but we note that the observed quantum yields (molecules of product/photon incident) are essentially unity for the alkene isomerization in the presence of $HSiEt_3$ using $[Co_2(CO)_6(P(OPh)_3)_2]$. Increased light intensity increases the observed rates, and we find that the linear pentenes can be equilibrated to the thermodynamic ratio in <3 h for a neat 1/1 $HSiEt_3$/1-pentene solution. The turnover rate thus exceeds 3×10^2/h, and may be much higher at higher intensities. If a 1/1 $HSiEt_3$/1-pentene is exposed to 10 psi H_2 and illuminated at high intensities the turnover number for pentane formation exceeds 10^2/h. Finally, at the high intensities, large yields of hydrosilation products are observable on the timescale of experiments detailed in Table II. Further data concerning these optical effects on turnover rate will be included in the full paper.

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10. Absi-Halabi, M.; Brown, T. L. J. Am. Chem. Soc., 1977, 99, 2982 provides evidence for $15e^-$-Co species from $17e^-$ fragments.

11. The oxidative addition of H_2 to Co(0) in the equilibrium $H_2 + N_2Co(PPh_3)_3 \rightleftharpoons N_2 + H_2Co(PPh)_3$, Speier, G.; Marko, L. Inorg. Chim. Acta, 1969, 3, 126, may be via $15e^-$ species. However, direct abstraction of H· from $HSiEt_3$ by the $17e^-$ radical may be possible if there is ligand redistribution to produce $[Co(CO)_nL_{4-n}]$ species; see also Kidd, D. R. and Brown, T. L. J. Am. Chem. Soc., 1978, 100, 4103.

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14. A reviewer suggested that $[CoL_4(olefin)]^+$ may represent an actual catalyst involved here. Small quantities of very active species are of course difficult to rule out, but $[CoL_4]^+$, though a reactive species, has a short lifetime and gives decomposition to $[CoL_5]^+$ and Co(O) under catalytic conditions: Muetterties, E. L.; Watson, P. L. J. Am. Chem. Soc., 1978, 100, 6978. Note too that we find photocatalytic formation of 3,3-dimethylpentane when $[Co_2(CO)_6(P(OPh)_3)_2]$ is irradiated in the presence of $HSiEt_3$/3,3-dimethyl-1-pentene evidencing catalytic activity for alkenes incapable of easy π-allyl-hydride formation believed to be important in the $[CoL_4]^+$ catalyzed isomerization. Use of $DSiEt_3$ results in the formation of $HSiEt_3$ and deuterated hydrocarbon alkane and alkene product.

Table I. Photocatalyzed 1-Pentene Reaction Using Dinuclear Co Complexes as Catalyst Precursors.

Catalyst Precursor, (conc.)	Conditions[a]	Irrdn Time, h	Analysis, %[b]			
			n-pentane	1-pentene	trans-2-pentene	cis-2-pentene
$[Co_2(CO)_6(P(n-Bu)_3)_2]$ ($2.64 \times 10^{-3}\underline{M}$)	$3.6\underline{M}$ 1-pentene in $\underline{n}$-octane	0	---	99.7	0.20	0.0_3
		94	---	99.7	0.2_3	0.0_9
		[thermal control]	---	99.7	0.2_1	0.0_6
	$1.0\underline{M}$ 1-pentene + $1.6 \times 10^{-2}\underline{M}$ P(OMe)$_3$ in $\underline{n}$-octane	0	---	99.7	0.1_8	0.1_6
		72	0.1_3	95.5	2.6_9	1.7_2
		[thermal control]	---	99.6	0.2_2	0.1_8
$[Co_2(CO)_6(P(OPh)_3)_2]$ ($8.97 \times 10^{-4}\underline{M}$)	$1.0\underline{M}$ 1-pentene in benzene	0	---	99.3	0.28	0.3_8
		76	0.2_8	92.0	5.0_5	2.65
		[thermal control]	---	99.3	0.4_0	0.3_0

[a] All experiments run at 25° C using 1.0 ml samples freeze-pump-thaw degassed in at least four cycles and hermetically sealed in Pyrex ampules. Irradiation was with a GE Blacklite with principal output at 355 nm ± 15 nm providing 1.6×10^{-6} ein/min incident on the sample.

[b] Analysis of C$_5$ mixture by vpc against $\underline{n}$-hexane as an internal standard.

Table II. Photocatalyzed 1-Pentene Reaction in the Presence of $HSiEt_3$.[a]

Catalyst Precusror, (conc.)	Conditions	Irrdn Time, h	Analysis, %			
			n-pentane	1-pentene	trans-2-pentene	cis-2-pentene
$[Co_2(CO)_6(P(n-Bu)_3)_2]$ (2.65 x 10^{-3} M)	3.6M $HSiEt_3$/ 3.6M 1-pentene (neat)	0	0.0_1	99.6	0.27	0.1_4
		94	3.1_0	3.30	74.5	18.0
		[thermal control]	0.6_4	97.9	1.0_7	0.3_6
	1.0M $HSiEt_3$ 1.0M 1-pentene in n-octane	52	0.93	94.0	3.61	1.51
	1.0M $HSiEt_3$ 1.0M 1-pentene 5.3x10^{-3} M $P(OMe)_3$ in n-octane	52	5.44	16.5	58.7	19.4
$[Co_2(CO)_6(P(OPh)_3)_2]$ (8.97 x 10^{-4} M)	1.0M $HSiEt_3$ 1.0M 1-pentene in benzene	0	---	99.6	0.28	0.20
		5	3.07	46.0	37.0	13.9
		[thermal control]	0.1_2	97.8	1.29	0.7_8
$[(\eta^5-C_5H_5)Fe(CO)_2-Co(CO)_3(P(OPh)_3)]$ (1.79 x 10^{-3} M)	1.0M $HSiEt_3$ 1.0M 1-pentene in benzene	0	---	99.6	0.2_2	0.2_0
		7	2.74	7.46	76.2	13.6
		[thermal control]	0.0_2	99.1	0.6_5	0.2_2
$[(\eta^5-C_5H_5)_2Fe_2(CO)_4]$ (2.65 x 10^{-3} M)	3.6M $HSiEt_3$ 3.6M 1-pentene (neat)	0	0.0_4	99.6	0.1_9	0.1_4
		96	0.77	98.3	0.6_0	0.3_5
		[thermal control]	0.0_4	99.3	0.4_1	0.2_5

[a] See notes for Table I.

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